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Selective Recovery of Cobalt, Nickel and Lithium from Sulfate Leachate of Cathode Scrap of Li-ion Batteries Using Liquid-Liquid Extraction

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This paper focuses on the extractive separation and selective recovery of cobalt, nickel and lithium from the sulfate leachate of cathode scrap generated during manufacture of lithium ion batteries (LIBs). The conditions for extraction, scrubbing and stripping of cobalt from nickel and lithium are optimized with an aqueous feed containing 25.1 $g{\cdot}dm^{-3}$ cobalt, 2.54 $g{\cdot}dm^{-3}$ nickel and 6.2 $g{\cdot}dm^{-3}$ lithium using Na-PC-88A. 99.8% Co is extracted with 60% Na-0.56 $mol{\cdot}dm^{-3}$ PC-88A in two counter-current stages at an O/A phase ratio of 3/1 and an equilibrium pH of 4.5. The "crowding effect" shown for the first time provides effective scrubbing of impurities (Ni and Li) with 2.0 $g{\cdot}dm^{-3}$ $CoSO_4$ solution. The McCabe–Thiele diagram predicts the scrubbing of 99.9% Ni and 99.9% Li at an equilibrium pH of 4.75 and O/A of 2/1 in two stages. High purity (99.9%) cobalt sulfate along with Ni and Li from the leach liquor of cathode scrap is recovered by solvent extraction. The proposed process ensures complete recycling of the waste of the manufacturing process of LIBs.

Key words: lithium ion batteries, cathode scrap, cobalt, recycling, solvent extraction, separation

1. INTRODUCTION

Nowadays, lithium ion batteries (LIBs) are extensively used as a power source for electronic devices rather than nickel-cadmium (Ni-Cd) or nickel-metal hydride (Ni-MH) batteries because of their advantages such as smaller size, higher energy density and battery voltage, and longer charging-discharging cycle [1,2]. The widespread and rapidly increasing production and consumption of LIBs have led to an increased battery scrap generation in both the production process and at the end-of-life stage. In spite of the fact that spent LIBs are generally not classified as dangerous waste, their inappropriate disposal may cause environmental problems due to the presence/generation of hazardous substances from flammable and toxic elements or compounds [3]. Therefore, recycling of spent LIBs through the recovery of the valuable metals contained in the cathode active material, such as cobalt, nickel and lithium, is becoming increasingly important to sustaining economical production and meeting the environmental regulations [2,3].

The recycling of valuable metals from spent LIBs mainly involves physical and chemical processes. Conventionally, physical processes comprise mechanical processing and thermal treatment while chemical processes cover acid or alkaline leaching, precipitation, solvent extraction and electrochemical recovery [2,4].

Because of the demand for high purity metals in the recycling of spent LIBs, more attention is focused on solvent extraction that meets the requirements for performance and economy in replacing the conventional separation processes involving precipitation methods. In the literature various hydrometallurgical processes using solvent extraction have been reported for the recovery of metal values from spent LIBs [5-19]. Zhang *et al.* [5] suggested using PC-88A (2-ethylhexylphosphonic acid mono-2-ethylhexyl ester) for the separation and recovery of cobalt and lithium in a mixed chloride solution from spent LIBs. This process provides high selectivity for cobalt over lithium and yields high purity metal products. However, the concentrated chloride system during leaching has some disadvantages in large scale operation due to its high corrosive nature. Swain *et al.* [8,10,11] investigated the use of saponified Cyanex 272 (bis(2,4,4-trimethylpentyl) phosphinic acid) to separate cobalt from lithium in sulfate solutions. Cobalt sulfate with > 99% purity can be prepared from mixed cobalt and lithium sulfate solutions

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using Na-Cyanex 272 as an extractant by controlling the stoichiometry suitably [8]. Kang *et al.* [12] reported a process for recovering cobalt sulfate from spent LIBs by reductive leaching and solvent extraction with Cyanex 272. Sulfuric acid and H_2O_2 were used in the leaching followed by precipitation of impurities, and selective extraction of cobalt using saponified Cyanex 272. Pranolo *et al.* [13] proposed a conceptual process flow-sheet for recovering cobalt, nickel and lithium from spent lithium ion battery leach solutions. The mixed extractant system containing Ionquest 801 and Acorga M5640 was used in the first solvent extraction circuit to remove impurities (Fe(III), Al (III), Cu(II)). Cyanex 272 was tested for further purification of cobalt, nickel and lithium in the second solvent extraction circuit. The advantage of this process is that cobalt and lithium can be effectively purified and recovered as separate products. However, this method suffers from the drawback of utilizing expensive extractants in scale-up and in industry, which leads to high initial plant investments. Despite having a better ability to separate cobalt and nickel, Cyanex 272 causes an increase in viscosity of the organic phase while exhibiting a decrease in the mass transfer rate in subsequent recycling in comparison to PC-88A.

Most chemical processes reported so far have mainly dealt with optimization for effective metal leaching, and have not ensured the complete separation and recovery of each metal from the spent LIBs. In particular, the above studies on the separation of cobalt and lithium employing solvent extraction are limited to the recycling of spent LIBs for the purpose of recovering only these two metals. Though lithium is vital for batteries and other industrial applications, and cobalt is a relatively expensive material compared to the other constituents, recovery of all metals is critical for effective recycling of LIBs. To date, scanty information is available regarding scrubbing of impurities from the loaded organic phase to achieve a high level of purity from the recovered metals [20,21].

Currently, the studies in our laboratory are directed towards the recycling of valuable metals from cathode scraps generated in the manufacturing process of LIBs. The process comprises several steps. First, the cathode scraps undergo heat treatment to completely liberate the cathodic materials ($LiCoO_3$) from aluminum foil. The cathodic materials are then leached in sulfuric acid in the presence of H_2O_2 to solubilize cobalt, lithium, iron, manganese, nickel, and aluminum. After oxidative precipitation of manganese selectively from the leach liquor with $KMnO_4$, and extraction of aluminum and iron using D2EHPA, the solution containing cobalt, lithium, and nickel needs to be further treated to recover these valuable metals.

In view of the above, this study aims at selectively recovering cobalt, nickel and lithium from sulfate leach liquor containing 25.1 $g{\cdot}dm^{-3}$ cobalt, 2.54 $g{\cdot}dm^{-3}$ nickel, and 6.2 $g{\cdot}dm^{-3}$ lithium obtained in the processing of cathode materials by solvent extraction using Na-PC-88A. We investigate the effect of the equilibrium pH and extractant concentration on the extractive separation of cobalt, nickel and lithium to arrive at the optimum conditions for recovering cobalt salt of high purity. In particular, we make a systematic study on scrubbing impurities from the loaded organic phase after extraction using a cobalt sulfate solution, which is the critical stage in obtaining a high purity cobalt product in the stripping stage. Such an investigation has not been described in previous reports. Factors affecting the scrubbing efficiency of nickel and lithium, such as the equilibrium pH, scrub solution concentration, and phase ratio, are also investigated here. Finally, cobalt in the loaded organic was stripped with diluted sulfuric acid. From the data obtained, a process flow-sheet is proposed showing its advantages, namely, simplicity, low operating cost, and recovery of highly pure metals from the sulfate leach liquor of the cathode scrap generated in the manufacturing process of LIBs.

2. EXPERIMENTAL PROCEDURES

2.1. Reagents and apparatus

Having been treated initially with $KMnO_4$ followed by D2EHPA to remove impurities such as Mn, and Al and Fe, the final leach liquor of the cathode scrap (pH 2.03) used for batch tests contained 25.1 $g{\cdot}dm^{-3}$ cobalt, 2.54 $g{\cdot}dm^{-3}$ nickel and 6.2 $g{\cdot}dm^{-3}$ lithium. The commercial extractant PC-88A was supplied by Daihachi Chemicals, Japan and was used without further purification. The extra pure kerosene oil supplied by Junsei Chemical Co., Japan (bp 453-543 K) was used as the diluent. The stock solution of the organic phase was prepared by diluting PC-88A in kerosene. The sodium form of the extractant was prepared by slowly adding a stoichiometric amount of 12 $mol{\cdot}dm^{-3}$ NaOH solution to the extractant in kerosene and stirring the phases to form a single phase. All the other chemicals were analytical grade reagents (Junsei Chemicals Co. Ltd). An atomic absorption spectrophotometer (Perkin Elmer model AAnalyst-400) and a pH meter (Orion 3-Star) were used to determine the metal concentrations and acidity of the solutions, respectively.

2.2. Solvent extraction procedure

Suitable volumes of aqueous and organic phases in a separating funnel were equilibrated by mechanical shaking for 600 seconds to attain the equilibrium. The pH of the aqueous phase was adjusted by adding diluted 0.10 $mol{\cdot}dm^{-3}$ NaOH or H_2SO_4. After phase disengagement, the aqueous phase was separated and its equilibrium pH was measured. The metal concentration in the aqueous phase was estimated by AAS after suitable dilution with 5.0% (v/v) HCl. The concentration of metals in the organic phase was calculated from the difference between the metal concentration in the aqueous phase before and after extraction. The analysis of the organic phase was carried out whenever necessary for which the organic phase was filtered through 1PS phase separation paper and a suitable

volume of aliquot was contacted three times with 2.0 mol·dm^{-3} HCl to transfer the metal to aqueous phase followed by its dilution and analysis by AAS.

The volume ratio of the aqueous and organic phases was kept at unity (O/A = 1/1) except in the McCabe–Thiele plots for extraction, scrubbing and stripping where the O/A ratio was varied in the range 1/5 to 5/1. All the experiments were carried out at room temperature (298 ± 1 K). The distribution ratio D was calculated as the concentration of metal present in the organic phase to that of the aqueous phase at equilibrium. From the D values, the percentage extraction (%E) and separation factor (β) were calculated using equations (1) and (2) [22].

$$\%E = \frac{D}{D+(V_{aq}/V_{org})} \times 100 \tag{1}$$

where V_{aq} and V_{org} are the volumes of aqueous and organic phases, respectively, and

$$\beta = \frac{D_{Co}}{D_{Ni}} = \frac{[\mathrm{Co}]_{org}/[\mathrm{Co}]_{aq}}{[\mathrm{Ni}]_{org}/[\mathrm{Ni}]_{aq}} \tag{2}$$

The scrubbing experiments were carried out by mixing a pure cobalt sulfate solution with the organic phase previously loaded using the procedure described for the extraction experiments. External pH control was not required during the scrubbing. For stripping studies, different concentrations of sulfuric acid solutions were used.

3. RESULTS AND DISCUSSION

3.1. Solvent extraction of cobalt

3.1.1. Effect of extractant concentration

The effect of extractant concentration on the extraction of cobalt, nickel and lithium was studied in the range 0.28-1.68 mol·dm^{-3} (PC-88A) while keeping the saponification to about 60% and the initial aqueous pH of 2.03. We observed that the extraction percentage of cobalt and nickel increased with an increase in the extractant concentration (Fig. 1). The cobalt extraction increased from 17.1 to 96.0% whereas it was 2.25 to 41.1% for nickel when the extractant concentration was increased from 0.28 to 1.68 mol·dm^{-3}. The increase of the extractant concentration, however, did not result in any significant increase in the extraction percentage of lithium.

The separation factor for cobalt over nickel ($\beta_{\mathrm{Co/Ni}}$) increased from 10.5 to 22.7 (Table 1) with an increase in the extractant concentration from 0.28-1.40 mol·dm^{-3} and decreased thereafter with a further increase in extractant concentration. The decrease in the separation factor above the extractant concentration of 1.40 mol·dm^{-3} was due to the increased co-extraction of nickel. The corresponding change in the equilibrium pH of the aqueous phase was in the range 4.06-4.63. For further experiments, 60% Na-0.56 mol·dm^{-3} PC-88A was chosen because of transfer of only a small amount of impurities (Ni and Li) into the organic phase.

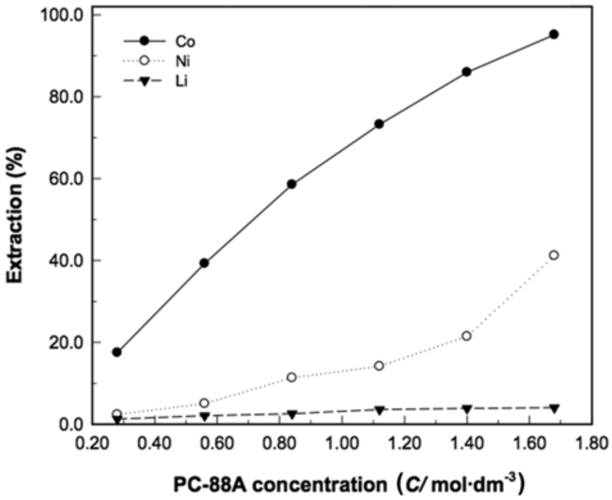

Fig. 1. Effect of PC-88A concentration on the extraction of cobalt, nickel and lithium. Organic phase: 60% Na-(0.28-1.68) mol·dm^{-3} PC-88A. Aqueous phase: 25.1 g·dm^{-3} cobalt, 2.54 g·dm^{-3} nickel and 6.2 g·dm^{-3} lithium; O/A = 1/1; contact time 600 seconds; temp. 298 K.

Table 1. Effect of Na-PC-88A concentration on separation factor of cobalt and nickel

60% Na-PC-88A (mol·dm^{-3})	Eq. pH	D_{Co}	D_{Ni}	$\beta = D_{\mathrm{Co}}/D_{\mathrm{Ni}}$
0.28	4.06	0.21	0.02	10.5
0.56	4.14	0.65	0.05	13.0
0.84	4.19	1.41	0.131	10.8
1.12	4.28	2.73	0.162	17.1
1.40	4.40	6.12	0.273	22.7
1.68	4.63	19.5	0.991	19.6

Organic phase: 60% Na-(0.28-1.68) mol·dm^{-3} PC-88A. Aqueous phase: 25.1 g·dm^{-3} cobalt, 2.54 g·dm^{-3} nickel and 6.2 g·dm^{-3} lithium; initial pH 2.03; O/A = 1/1; contact time 600 sec; temp. 298 K.

3.1.2. Effect of equilibrium pH

Extraction of cobalt, nickel and lithium was studied in the equilibrium pH range 1.00-5.50 from the same aqueous feed using 60% Na-0.56 mol·dm^{-3} PC-88A. The results are plotted in Fig. 2 as the percentage extraction vs the equilibrium pH. The extraction of lithium was almost constant regardless of the equilibrium pH, whereas extraction of cobalt and nickel increased with an increase in the equilibrium pH. In particular, the increase in extraction was appreciable for cobalt but not so much for nickel, which demonstrates the selectivity for cobalt within the range of the investigated equilibrium pH. The highest separation factors $\beta_{\mathrm{Co/Ni}}$ and $\beta_{\mathrm{Co/Li}}$ were 10.8 and 11.7, respectively, at an equilibrium pH of 4.5. We may thus conclude that the most appropriate equilibrium pH for cobalt is 4.5, which facilitates the high metal extraction and selectivity. A pH above 6.0 is not desirable because it causes pre-

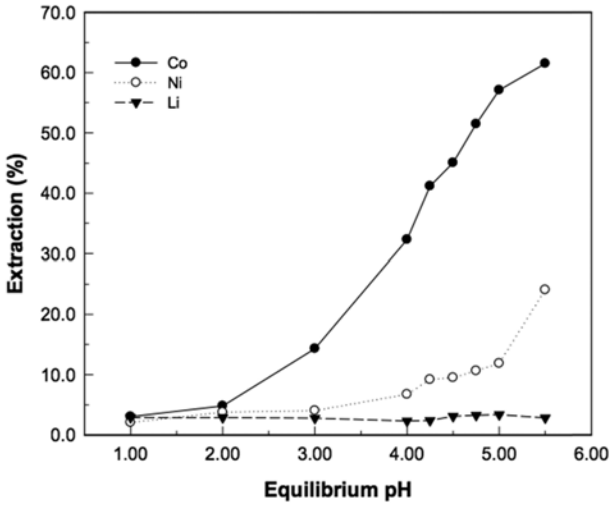

Fig. 2. Effect of equilibrium pH on the extraction of cobalt, nickel and lithium. Organic phase: 60% Na-0.56 mol·dm^{-3} PC-88A. Aqueous phase: 25.1 g·dm^{-3} cobalt, 2.54 g·dm^{-3} nickel and 6.2 g·dm^{-3} lithium; O/A = 1/1; contact time 600 sec; temp. 298 K.

cipitation of cobalt hydroxide and third phase formation, which is related to the high viscosity of the organic phase [23,24].

3.1.3. Extraction isotherm and counter-current simulation

The cobalt extraction isotherm was determined by varying the O/A phase ratio from 1/5 to 5/1 at an equilibrium pH of 4.5 using 60% Na-0.56 mol·dm^{-3} PC-88A and the McCabe–Thiele diagram was constructed (Fig. 3). Three theoretical extraction stages are needed for extraction of cobalt at an O/A ratio of 2.5/1. Increasing the O/A ratio causes a decrease in the number of stages for cobalt extraction. At O/A = 3/1,

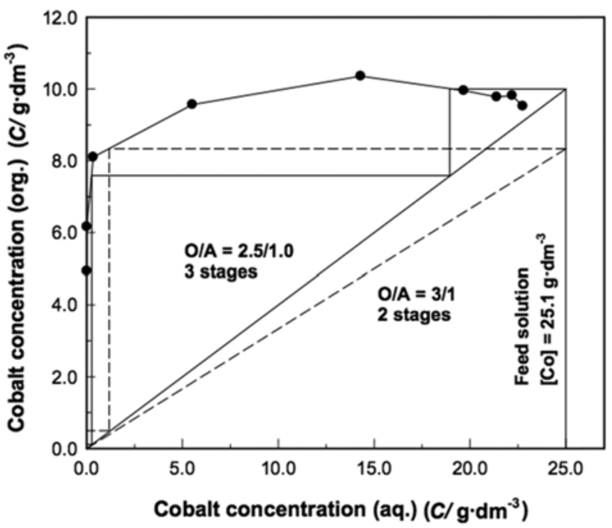

Fig. 3. McCabe–Thiele diagram for cobalt extraction. Organic phase: 60% Na-0.56 mol·dm^{-3} PC-88A. Aqueous phase: 25.1 g·dm^{-3} cobalt, 2.54 g·dm^{-3} nickel and 6.2 g·dm^{-3} lithium; O/A from 1/5 to 5/1; contact time 600 sec; temp. 298 K; pH = 4.5.

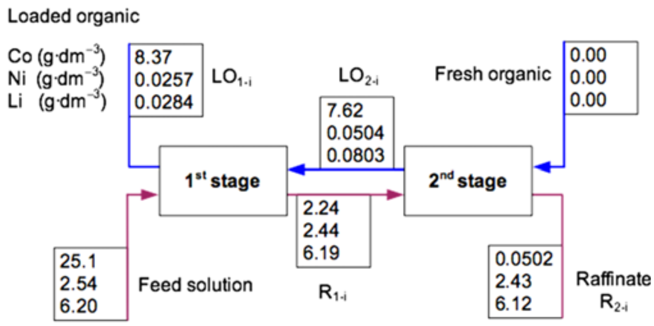

Fig. 4. Two-stage counter-current simulation study for extraction of cobalt, nickel and lithium. Organic phase: 60% Na-0.56 mol·dm^{-3} PC-88A. Aqueous phase: 25.1 g·dm^{-3} cobalt, 2.54 g·dm^{-3} nickel and 6.2 g·dm^{-3} lithium; O/A = 3/1; equilibrium pH 4.5; contact time 600 sec; temp. 298 K.

two stages are required for quantitative cobalt extraction.

To confirm the McCabe–Thiele prediction, a two-stage counter-current simulation study was undertaken using 60% Na-0.56 mol·dm^{-3} PC-88A at O/A = 3/1 and an equilibrium pH of 4.5. The equilibrium concentrations of related metals in the aqueous and organic phases after each extraction stage are shown in Fig. 4. The final raffinate (R_{2-i}) contained 0.0502 g·dm^{-3} cobalt corresponding to the recovery of cobalt into the organic phase to 99.8% at a purity of 99.3%; extraction of other metals was only 4.3% nickel and 1.3% lithium. These results were quite promising because in practice, higher purities could be achieved by the additional extraction stages and/or providing scrubbing stages. Analysis of the loaded organic (LO_{1-i}) containing 8.37 g·dm^{-3} cobalt and 0.0257 g·dm^{-3} nickel and 0.0284 g·dm^{-3} lithium apparently confirmed the mass balance of these metals. For a phase ratio (O/A) of 3/1, the concentration of metals in the organic phase was one third that of the aqueous phase.

3.2. Scrubbing impurities from loaded organic

3.2.1. Scrubbing reagent selection and effect of equilibrium pH

The loaded organic (8.37 g·dm^{-3} Co; 25.7 mg·dm^{-3} Ni; 28.4 mg·dm^{-3} Li) used for nickel and lithium scrubbing was obtained from a two-stage counter-current simulation study at these conditions: 60% Na-0.56 mol·dm^{-3} PC-88A, O/A = 3/1, and an equilibrium of pH 4.5. To pursue the objective, scrubbing can be accomplished by two approaches.

In the first method, diluted sulfuric acid solutions at a unit phase ratio was investigated in an equilibrium pH range of 5.0-3.0, which resulted in a scrubbing efficiency of 64.3-81.2% Ni, 89.2-95.2% Li and co-scrubbing of 3.43-53.6% Co. Lithium was thus efficiently removed from the organic phase, but taking into account the nickel and cobalt concentrations, the results obtained were not so promising since the removal of impurities was only achieved with a simultaneous loss of cobalt.

The second method for scrubbing nickel and lithium was attempted using cobalt sulfate solutions. The cation exchange

reaction between cobalt and metal impurities in the organic phase was expected to be similar to that of the mechanism reported by Zhang *et al*. [5] and shown in equations (3) and (4):

$$NiA_{2(org.)} + Co^{2+}{}_{(aq.)} = CoA_{2(org.)} + Ni^{2+}{}_{(aq.)} \quad (3)$$

$$2LiA_{(org.)} + Co^{2+}{}_{(aq.)} = CoA_{2(org.)} + 2Li^{2+}{}_{(aq.)} \quad (4)$$

Cobalt in the scrub liquor is not intended to load in the organic phase, but rather to replace the metal impurities. The cobalt-depleted scrub liquor may be directed to the extraction circuit. It is noted that pH control during scrubbing process is not required because scrub liquor is pre-adjusted to the desired pH value. The cobalt at this stage does not exchange hydrogen ions, but other metal impurities, and therefore, the pH remains constant.

The pH of the scrubbing solution containing 2.0 g·dm^{-3} Co was varied in the range 3.75-6.5. The scrubbing tests were performed at an A/O ratio of 1:1 and 298 K. The effect of the equilibrium pH on the nickel and lithium scrubbing efficiencies is given in Table 2. A higher nickel scrubbing efficiency was obtained at a lower pH, whereas lithium scrubbing was almost complete (>99%) within the investigated pH range. For instance, when the scrub pH decreased from 6.5 to 3.75, the nickel scrubbing efficiency increased from 67.6 to 95.2%.

A great deal of attention needs to be paid in scrubbing impurities at lower pH which would lead to higher cobalt concentration in the loaded scrub solution, and consequently, more cobalt recycling to the extraction stages would be required in a continuous process. When the scrub pH was decreased from 4.65 to 4.17, the cobalt concentration in the loaded scrub liquor was almost doubled, that is from 2.07 to 4.02 g·dm^{-3} corresponding to the loss of 24.1% cobalt in the scrubbed organic phase.

When the equilibrium pH was increased from 4.75 to 6.50, more cobalt was loaded into the organic phase, thereby decreasing the cobalt concentration from 1.96 g·dm^{-3} to 0.0301 g·dm^{-3} in the scrub solution which was to be recycled. This would, however, require more stages of scrubbing nickel due to the low scrubbing efficiency at a higher pH. Thus, the equilibrium pH for scrubbing Li and Ni from cobalt-loaded organic was chosen to be 4.75 in subsequent experiments.

3.2.2. Effect of $CoSO_4$ concentration

Experiments were conducted to determine the effect of cobalt sulfate concentration on the scrubbing of nickel and lithium at an equilibrium pH of 4.75 and an O/A phase ratio of 1:1. The data in Table 3 show that the scrubbing efficiency of nickel increased from 65.0 to 93.4% when the concentration of cobalt was increased from 0.2 to 3.0 g·dm^{-3}, which was 87.7% at scrub feed of 2.0 g·dm^{-3} Co. The lithium scrubbing efficiency was, however, approximately 99.9% irrespective of the cobalt concentration. These results are clear evidence of the "crowding effect" during the scrubbing process with a higher concentration of cobalt sulfate.

In fact, the scrubbing process with the utility of cobalt sulfate is very complicated and may comprise many exchange reactions, such as Ni_{org}/Co^{2+}, Li_{org}/Co^{2+}, Ni_{org}/H^{+}, Co_{org}/H^{+}. However, we noted that the final pH of the scrubbing solutions remained constant at 4.75 before and after scrubbing regardless of the cobalt concentration. This clearly confirms that the exchange reactions Ni_{org}/H^{+} and Co_{org}/H^{+} are negligible during the scrubbing process. In addition, the scrubbing of lithium as mentioned above does not strongly rely on the concentration of cobalt in the scrubbing solution. Therefore, to simplify the system, only the Ni_{org}/Co^{2+} exchange reaction should be taken into account. The amount of nickel substituted by cobalt can be calculated as in Eq. (5):

$$S_{Ni/Co} = \frac{[Ni]_{LO} - [Ni]_{SBO}}{[Co]_{SBO} - [Co]_{LO}} \times 100\% \quad (5)$$

where $S_{Ni/Co}$ represents the percentage of cobalt replacing nickel in the organic solution during scrubbing. $[Ni]_{LO}$, $[Co]_{LO}$,

Table 2. Effect of equilibrium pH on the scrubbing efficiency of nickel and lithium using cobalt sulfate solution

Eq. pH	Metal in scrubbed organic			Metal in loaded scrub liquor			SB_{Ni} (%)	SB_{Li} (%)
	Co (g·dm^{-3})	Ni (mg·dm^{-3})	Li (mg·dm^{-3})	Co (g·dm^{-3})	Ni (mg·dm^{-3})	Li (mg·dm^{-3})		
3.75	3.93	0.762	0.0204	6.44	24.9	28.3	95.2	99.9
4.02	5.48	0.951	0.145	4.88	24.7	28.2	93.9	99.2
4.17	6.35	1.17	0.101	4.02	24.5	28.3	92.5	99.5
4.45	7.42	1.21	0.114	2.95	24.5	28.2	92.3	99.4
4.65	8.29	1.33	0.132	2.07	24.4	28.2	91.5	99.3
4.75	8.48	1.46	0.163	1.96	24.2	28.2	90.7	99.1
5.00	9.14	1.59	0.144	1.22	24.1	28.2	89.9	99.2
5.25	9.82	1.88	0.171	0.55	23.8	28.2	88.0	99.1
5.50	10.1	2.02	0.192	0.271	23.7	28.2	87.1	99.0
6.00	10.3	2.05	0.213	0.102	23.6	28.2	86.9	98.9
6.50	10.3	5.08	0.194	0.0301	20.6	28.2	67.6	99.0

LO: 8.37 g·dm^{-3} cobalt, 25.7 mg·dm^{-3} nickel and 28.4 mg·dm^{-3} lithium. Aqueous phase: 2.0 g·dm^{-3} $CoSO_4$; O/A = 1/1; contact time 600 sec; temp. 298 K.

Table 3. Effect of cobalt sulfate solution on the scrubbing efficiency of nickel and lithium

Scrubbing solution $CoSO_4$ ($g \cdot dm^{-3}$)	Metal in scrubbed organic			Metal in loaded scrub liquor			SB_{Co} (%)	SB_{Ni} (%)	SB_{Li} (%)
	Co ($g \cdot dm^{-3}$)	Ni ($mg \cdot dm^{-3}$)	Li ($mg \cdot dm^{-3}$)	Co ($g \cdot dm^{-3}$)	Ni ($mg \cdot dm^{-3}$)	Li ($mg \cdot dm^{-3}$)			
0.2	8.04	8.99	0.801	0.532	16.7	27.9	3.89	65.0	97.2
0.5	8.07	7.85	0.692	0.803	17.8	28.0	3.53	69.4	97.6
1.0	8.08	6.82	0.411	1.21	18.9	28.3	3.45	73.4	98.6
1.5	8.08	5.66	0.210	1.79	20.0	28.5	3.44	77.9	99.3
2.0	8.41	3.17	0.0414	1.96	22.6	28.7	– 0.512*	87.7	99.9
2.5	8.71	2.13	0.0302	2.22	23.7	28.7	– 3.33*	91.7	99.9
3.0	9.22	1.71	0.0104	2.11	24.1	28.7	– 10.6*	93.4	99.9

*minus values denote that cobalt was more loaded into the organic phase
LO: 8.37 $g \cdot dm^{-3}$ cobalt, 25.7 $mg \cdot dm^{-3}$ nickel and 28.4 $mg \cdot dm^{-3}$ lithium. Aqueous phase: 0.2-3.0 $g \cdot dm^{-3}$ $CoSO_4$; O/A = 1/1; contact time 600 seconds; temp. 298 K; equilibrium pH 4.75.

$[Ni]_{SBO}$, $[Co]_{SBO}$ indicate the concentrations of nickel and cobalt in the loaded organic solution and in the scrubbed organic solution, respectively.

Calculation of the substitution efficiency ($S_{Ni/Co}$) is meaningful in optimizing the cobalt concentration in scrubbing for commercial scale. For example, the calculated $S_{Ni/Co}$ values at a cobalt concentration of 2.0, 2.5 and 3.0 $g \cdot dm^{-3}$ were 50.6, 7.72, and 2.05%, respectively. The steep decline in substitution efficiency at a higher cobalt sulfate concentration meant more cobalt loading into the organic phase while the scrubbed nickel almost reached equilibrium. Therefore, scrubbing with a high concentration of cobalt sulfate is not promising in terms of reducing the cost of operation. Taking into account the $S_{Ni/Co}$ value and cobalt concentration in the loaded scrub liquor, we chose a solution of 2.0 $g \cdot dm^{-3}$ cobalt sulfate for further studies.

3.2.3. Scrubbing isotherm

The scrubbing isotherm of nickel and lithium with a 2.0 $g \cdot dm^{-3}$ cobalt sulfate solution was determined using the phase ratio method (O/A: 1/5 to 5/1), and the McCabe–Thiele diagram is presented in Fig. 5. The scrubbing of lithium was very effective and was independent of a varying phase ratio, whereas the scrubbing efficiency for nickel increased from 53.9 to 99.9% with a decrease in the O/A ratio from 5/1 to 1/5. In fact, a higher O/A ratio is preferred to decrease the amount of scrub solution that can be recycled to the extraction process, though more stages may be required due to low scrubbing efficiency. The isotherm predicted two counter-current stages for completely scrubbing nickel and lithium at an O/A phase ratio of 2:1; the nickel scrubbing efficiency can be expected to be 87.7 and 99.9% in the first and second stage, respectively. In a two-stage counter-current simulation the scrubbed organic with less than 1.5 $mg \cdot dm^{-3}$ nickel and lithium was obtained, indicating almost quantitative scrubbing of the impurities. Due to the "crowding effect" mentioned above, the concentration of cobalt in the scrubbed organic increased to 8.41 $g \cdot dm^{-3}$ while that of nickel and lithium decreased to 1.46 $mg \cdot dm^{-3}$ and 0.16 $mg \cdot dm^{-3}$, respectively. The scrubbed organic was collected and used for stripping studies.

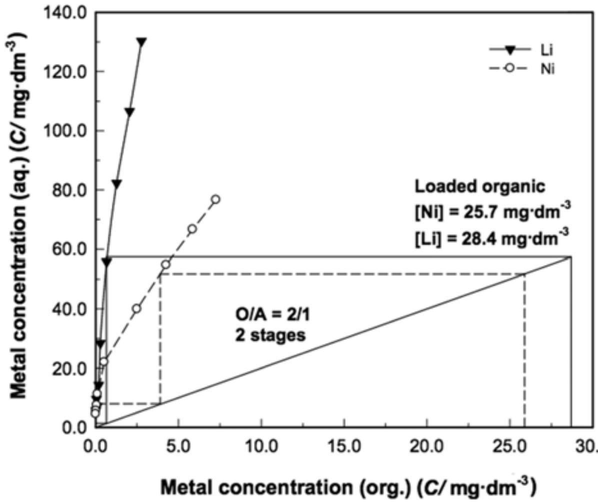

Fig. 5. McCabe–Thiele diagram for nickel and lithium scrubbing from the loaded organic. LO: 8.37 $g \cdot dm^{-3}$ cobalt, 25.7 $mg \cdot dm^{-3}$ nickel and 28.4 $mg \cdot dm^{-3}$ lithium. Aqueous phase: $CoSO_4$ 2.0 $g \cdot dm^{-3}$; O/A from 1/5 to 5/1; contact time 600 sec; temp. 298 K.

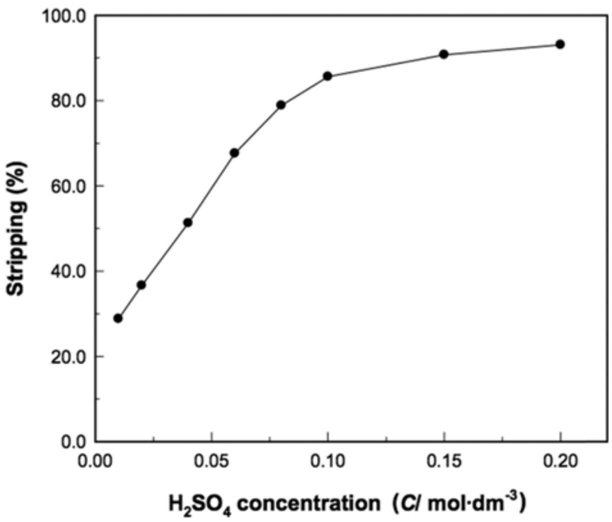

Fig. 6. Effect of acid concentration on stripping of cobalt from loaded organic. LO: 8.41 $g \cdot dm^{-3}$ cobalt, 1.46 $mg \cdot dm^{-3}$ nickel and 0.16 $mg \cdot dm^{-3}$ lithium. Aqueous phase: H_2SO_4 0.01-0.2 $mol \cdot dm^{-3}$; O/A = 1/1; contact time 600 sec; temp. 298 K.

3.3. Stripping of cobalt from the loaded organic

Various concentrations of sulfuric acid (0.01-0.2 mol·dm^{-3}) were used for cobalt stripping from the scrubbed organic at an equal phase ratio in 600 seconds. The results of the stripping efficiency of cobalt, nickel and lithium are shown in Fig. 6. The stripping of cobalt increased from 28.8 to 93.1% with a rise in acid concentration from 0.01-0.2 mol·dm^{-3}. In spite of the fact that almost all the nickel and lithium left out in the organic phase after the scrubbing process was co-stripped, the process is adequate to achieve the initial target of high purity cobalt recovery because of a very low concentration of the impurities. Therefore, a solution of 0.2 mol·dm^{-3} sulfuric acid was chosen for further studies.

The McCabe–Thiele plot for stripping cobalt from the loaded PC-88A (Fig. 7) was also constructed with 0.2 mol·dm^{-3} H_2SO_4 by varying the O/A ratio from 1/5 to 5/1 while maintaining the total volume of phases constant. The data suggested two stages for complete cobalt stripping at an O/A ratio of 1/1. Therefore, two-stage counter-current cobalt stripping studies were carried out at an O/A ratio of 1/1 using 0.2 mol·dm^{-3} H_2SO_4 to confirm the data predicted in the isotherm (Fig. 8).

The concentration of three metals in the strip liquor and regenerated organic phase during the simulation is highlighted in Fig. 8. The equilibrium state for the counter-current stripping system was achieved after three cycles of contact (data not shown). The final concentration of cobalt in strip liquor $ST_{1\text{-}i}$ was analyzed to be 8.41 g·dm^{-3}, while nickel and lithium co-stripped were 1.46 mg·dm^{-3} and 0.16 mg·dm^{-3}, respectively. Apparently, recovered cobalt has a high purity of 99.9% with only 0.08% nickel and 0.01% lithium content. The cobalt stripping efficiency in the first and second stage was determined to be 90 and 99.8%, respectively.

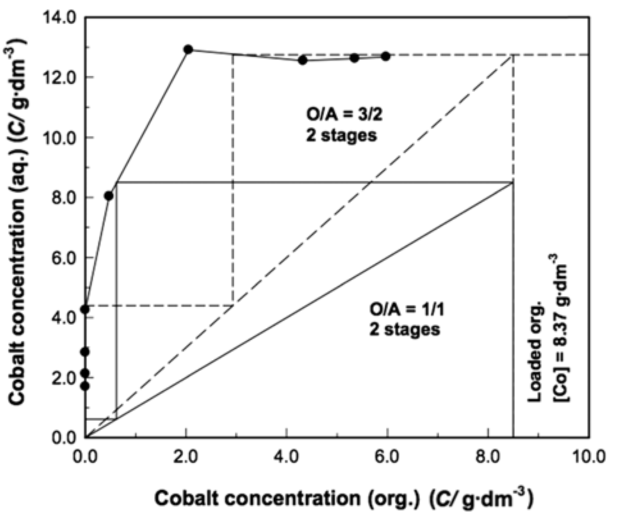

Fig. 7. McCabe–Thiele diagram for cobalt stripping from the loaded organic. LO: 8.41 g·dm^{-3} cobalt, 1.46 mg·dm^{-3} nickel and 0.16 mg·dm^{-3} lithium. Aqueous phase: H_2SO_4 0.2 mol·dm^{-3}; O/A from 1/5 to 5/1; contact time 600 sec; temp. 298 K.

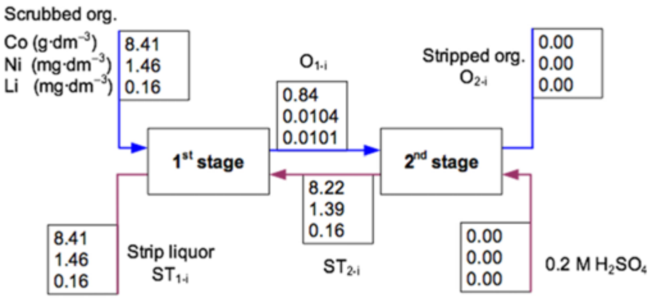

Fig. 8. Two-stage counter-current simulation study for the stripping of cobalt from loaded organic. LO: 8.41 g·dm^{-3} cobalt, 1.46 mg·dm^{-3} nickel and 0.16 mg·dm^{-3} lithium. Aqueous phase: 0.2 mol·dm^{-3} H_2SO_4; O/A = 1/1; contact time 600 sec; temp. 298 K.

3.4. Nickel recovery from the raffinate

The raffinate after cobalt extraction containing 2.43 g·dm^{-3} Ni and 6.12 g·dm^{-3} Li can be treated to recover nickel in two different ways, (i) using solvent extraction, and (ii) precipitation as nickel hydroxide.

An organic phase of 5.0% (v/v) PC-88A was equilibrated with the feed solution at an equilibrium pH of 6.00. Over 99.9% nickel was recovered while only 0.01% lithium was co-extracted. In the case of the precipitation method, the equilibrium pH of the raffinate was adjusted to different values (from 5.0 to 9.0) using 1.00 mol·dm^{-3} NaOH. The results showed that the precipitation of nickel increased with an increase in equilibrium pH with a quantitative precipitation of nickel hydroxide (96.7% purity) and a loss of only 1.33% lithium at a pH of 8.5. The solution after filtration was collected and used for lithium recovery.

Each of the above two methods for nickel recovery has its own advantages and disadvantages. The precipitation method is simpler and cheaper than the solvent extraction. However, solvent extraction with PC-88A has a high selectivity and the final product is in the form of nickel sulfate with a higher purity of 99.8%.

3.5. Recovery of lithium using sodium carbonate

The solution remaining after nickel precipitation and/or nickel extraction was treated with a saturated sodium carbonate solution to precipitate lithium in the form of lithium carbonate (Eq. (6)).

$$Li_2SO_4 + Na_2CO_3 = Li_2CO_3 + Na_2SO_4 \quad (6)$$

The temperature for the reaction was maintained at 398 K to minimize solubility loss due to the fact that Li_2CO_3 solubility decreases from 1.52 to 0.71 g/100 g H_2O with an increase in temperature from 298 to 398 K [25].

A trace amount of nickel remaining in the mother liquor was also co-precipitated along with lithium. Therefore, the lithium carbonate was filtrated and washed with hot water to remove the impurity. The analytical results showed that 92%

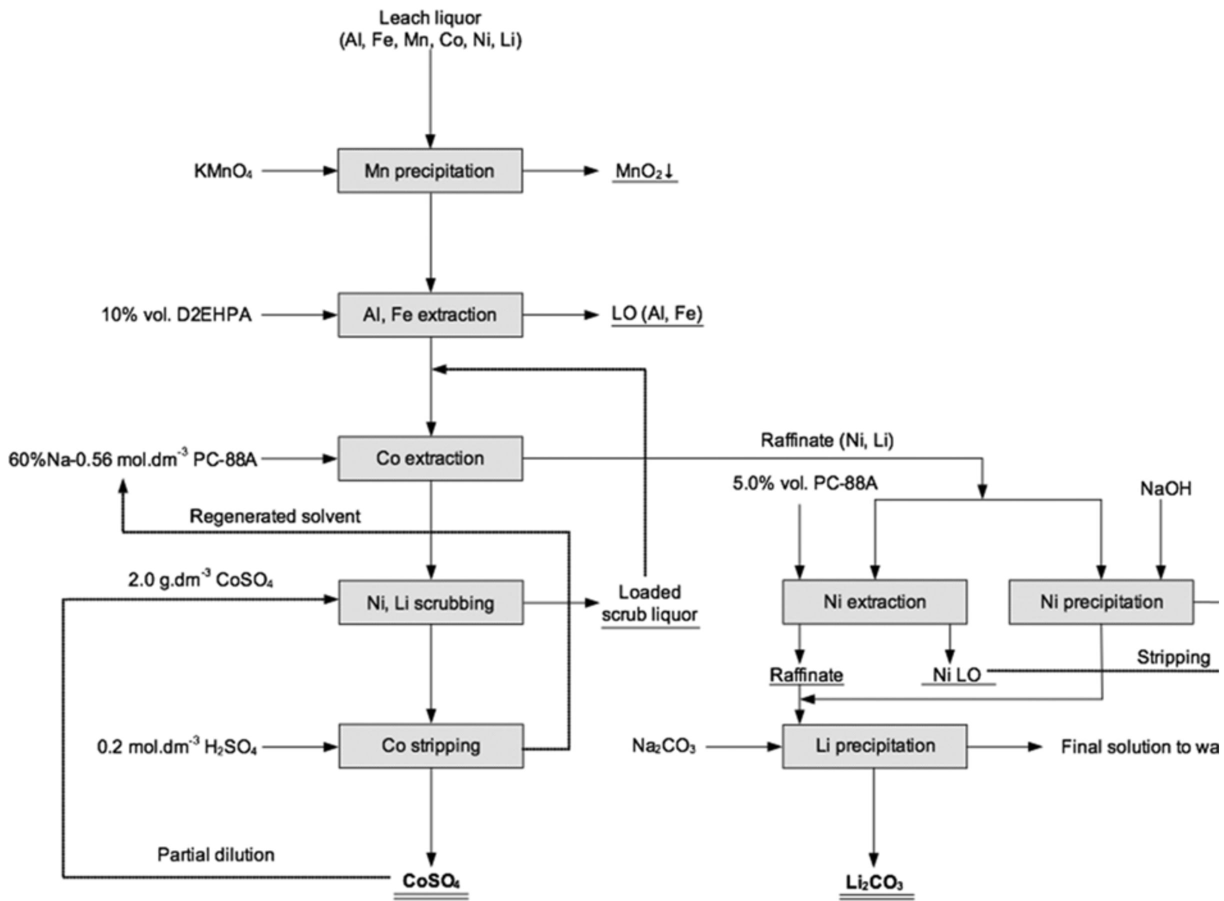

Fig. 9. Flow-sheet of the process for the recovery of cobalt, nickel and lithium from sulfate leach liquor of the cathode scrap generated in the manufacturing process of Li-ion batteries.

of the lithium was recovered as a precipitate while the content of nickel in the precipitate was less than 0.05%. After recovering the three metals, the waste solution was neutralized before discharging the effluents into the environment.

3.6. Flow-sheet for the recovery of metals

Based on the above data, we developed a flow-sheet of the process for the recovery of cobalt, nickel and lithium from the sulfate leach liquor of the cathode scrap generated in the manufacturing process of LIBs (Fig. 9). Some of the key advantages of this process is its simplicity, selective metal separation, and low operating cost to meet the demand for high-purity cobaltproducts.

The manganese in the leach liquor can first be removed as insoluble manganese oxide with the addition of $KMnO_4$ as mentioned previously. The oxidative precipitation of manganese is highly selective at room temperature within the equilibrium pH range of 2.0-3.0. Moreover, the precipitated manganese oxide is expected to be relatively pure and may need minimum purification. Aluminum and iron can then be selectively separated from nickel, cobalt and lithium using 10% (v/v) D2EHPA at an equilibrium pH of 2.5. No pH adjustment is required during separation of aluminum and iron, which results in decreased processing cost.

The solution containing cobalt, nickel and lithium can be further treated for cobalt separation with 60% Na-0.56 mol·dm^{-3} PC-88A at an equilibrium pH of 4.5. A small amount of nickel and lithium co-extracted into the organic phase is removed by scrubbing with a 2.0 g·dm^{-3} cobalt sulfate solution. The selective scrubbing of these impurities is associated with the "crowding effect" of cobalt replacing nickel and lithium in the organic phase. Cobalt as sulfate of high-purity (99.9%) is recovered using 0.2 mol·dm^{-3} H_2SO_4. The raffinate containing nickel and lithium after cobalt extraction can be treated in two different ways using solvent extraction with 5.0% (v/v) PC-88A or the precipitation method for nickel separation and recovery. Finally, sodium carbonate can be used for the precipitation of lithium in the form of lithium carbonate at high temperature (398 K).

4. CONCLUSIONS

Based on the results of our studies, we make the following conclusions.

(1) High-purity cobalt (99.9%) in solution can be recovered from the sulfate leach liquor of the cathode scrap generated in the manufacturing process of LIBs by the solvent extraction using the sodium salt of PC-88A.

(2) The cobalt, nickel and lithium extraction efficiency and separation factor depend upon the extractant concentration and the equilibrium pH of the aqueous phase. An extractant concentration of 60% Na-0.56 mol·dm^{-3} PC-88A was found to be suitable for selective cobalt extraction.

(3) The prediction of the McCabe–Thiele plot showing the requirement of two stages for counter-current extraction of cobalt with 60% Na-0.56 mol·dm^{-3} PC-88A at an aqueous phase equilibrium pH of 4.5 and an O/A phase ratio of 3/1 was confirmed in a simulation study. An almost quantitative extraction of cobalt was achieved under these conditions.

(4) The purification of a loaded organic phase containing 8.37 g·dm^{-3} Co; 25.7 mg·dm^{-3} Ni; 28.4 mg·dm^{-3} Li was successfully achieved by scrubbing with cobalt sulfate solution. The "crowding effect" of cobalt was proved effective in providing a driving force to scrub nickel and lithium (metal impurities) from the loaded organic phase by displacing them.

(5) Nickel and lithium were quantitatively scrubbed with a 2.0 g·dm^{-3} cobalt sulfate solution at an O/A of 2:1 and an equilibrium pH of 4.75 in two counter-current stages.

(6) Stripping of cobalt from the loaded organic with 0.2 mol·dm^{-3} H_2SO_4 resulted in over 99.9% stripping efficiency in the two-stage counter-current at an O/A ratio of 1:1.

(7) The proposed process flow-sheet is simple and has the advantage of recovering extremely pure cobalt, nickel and lithium salts from the sulfate leach liquor of the cathode scrap produced in the manufacturing process of LIBs.

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